Indian J. Phys. **44**, 325–329, (1970)

Use of a logarithmic form of potential in the studies on metals

By J. Behari

Department of Physics, Indian Institute of Technology, Hauz Khas, New Delhi-29, India

(*Received*, 20 *November* 1969)

A new logarithmic form of central potential between a pair of atoms is proposed for metals. Calculations on cohesive energies for several FCC, BCC, and HCP metals are reported and are found to be in good agreement with experimental data in all the cases.

Introduction

One approach to the theoretical study of the properties of solids is through the assumption of a central pairwise potential function. Unfortunately, the calculation of the potential energy of an assembly of given particles as a function of their mutual distance is very difficult and it has been solved by quantum mechanical methods in a few cases only (Mott & Jones 1936, Seitz 1940, Kuhn & Van Vleck 1950, Kambe 1955, Nikulin 1966). However, if we assume the lattice structure, lattice constant and the lattice energy, a satisfactory explanation can be presented of various lattice dynamical and thermodynamical properties of solids, within the range of approximation, by supposing a force law, provided it resembles the real one in some general features. The parameters of the potential function are determined by fitting it in a narrow region surrounding the equilibrium point, for the structure generally remains unaltered and the density changes slightly even at high pressure and upto the melting point. Most of the properties of the solids are determined by points near the minima of the potential energy curve. Those points, therefore, which are farther away from the minimum point will not affect the results as long as the chosen parameters retain the general feature of the curve. By the same reasoning it can be assumed that ϕ depends on the mutual distance of the particles only, even in those cases where the interatomic forces are not central as, for example in metals.

If $\phi(r)$ is the energy of interaction of two atoms at a distance r apart, then for $\phi(r)$ to represent a true interaction potential in a solid, it must satisfy the following conditions (Girifalco & Weizer 1959) :

i) The derivative of potential $\phi(r)$ (*i.e.* $(\partial\phi/\partial r)$) must have attractive nature for large r, and repusive for small r, hence should have minimum at $r = r_0$ (equilibrium separation).

ii) The decrease in $\phi(r)$ with r should be more rapid than r^{-3}.

These conditions are consequence of simple physical considerations; the first is due to the existence of condensed phases and the second only confirms that the cohesive energy is finite. The two together mean that the crystal structure be stable under infinitesimal homogeneous deformation.

Born and his collaborators (1940) have made a detailed analysis of the stability of crystal lattices and have given conditions that must be satisfied among the elastic constants. For cubic crystals these are :

iii) All elastic constants are positive,

iv) $C_{11}-C_{12} > 0.$

A good potential must have a minimum number of parameters, yet predict the remaining constants with sufficient accuracy as well as being adequately close to the dispersion forces at large distance. For metals, three potential energy functions have been used by different workers;

1. The Mie-Gruneisen potential

$$\phi(r) = -\frac{A}{r^n} + \frac{B}{r^m}, \quad (n < m),$$

which assumes that the interatomic force is a superposition of an attracting and a repelling force, both depending on the distance by a simple inverse power function. Gruneisen employed this function in his early investigations on the theory of solids. Furth (1944) and afterwards Dayal & Sharma (1955) and Cole (1959) have discussed the applicability of this function for a number of solids.

2. The Morse potential (Morse 1929)

$$\phi(r) = D[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}],$$

originally suggested for molecules, has also been used for metals (Girifalco & Weizer 1959) where α is a constant and D is the dissociation energy.

3. Rydberg (1931) proposed the following function for diatomic molecules

$$\phi(r) = -D[1+b(r-r_0)]e^{-b(r-r_0)}$$

where b is a constant. This potential has the shape appropriate for a potential function and has been found to give better results than the Morse potential for a good number of diatomic molecules. It has also been successfully applied in the studies of metals (Varshni & Bloore 1963).

Apart from being cumbersome to calculate, Rydberg potential as also Morse suffers from one disadvantage, as being finite for $r = 0$. Recently Prakash & Behari (1969) proposed a logarithmic form of potential for the exchange interaction between ions in alkali halides, and it was found that the calculation of

cohesive energy yields an excellent agreement with the experimental data. It removed the physical drawback with the most acceptable Born form ($ae^{-r/\rho}$) *viz.* $\phi_{repulsive}$ = constant, rather than infinity, for $r = 0$.

Logarithmic Function for Metals

In view of this we propose a new form for the potential in metals which satisfies the physical condition at $r = 0$ and has steeper slope than the exponential form :

$$\phi(r) = -A_1 \log_e[1+(B_1/r)^n]+A_2 \log_e[1+(B_2/r)^m]$$

It involves six constants, namely A_1, B_1, A_2, B_2, n and m.To reduce the number of unknown parameters we have chosen $B_1 = B_2$, the ionic radii of the metal in question, which are taken from the work of Pauling (1963). n and m are generally chosen from the work of Furth (1944). The remaining two constants A_1 and A_2 are obtained by applying the condition of crystal stability

$$\left(\frac{\partial\phi}{\partial r}\right)_{r=r_0} = 0$$

and the compressibility

$$\left(\frac{\partial^2\phi}{\partial r^2}\right)_{r=r_0} = \frac{9kr_0}{\beta_0},$$

where β = compressibility, k the structure factor and the zero subscript refers to the values of parameters at absolute zero of temperature. Expressions for A_2 and A_1 are

$$A_2 = \frac{9kr_0/\beta_0}{\dfrac{B_2{}^m m}{r_0{}^{m+1}+B_2{}^m r_0}\left[\dfrac{(m+1)r_0{}^m+B_2{}^m}{r_0{}^{m+1}+B_2{}^m r_0} - \dfrac{(n+1)r_0{}^n+B_1{}^n}{r_0{}^{n+1}+B_1{}^n r_0}\right]}$$

and

$$A_1 = \left(\frac{A_2 B_2{}^m m}{r_0{}^{m+1}+B_2{}^m r_0}\right)\left(\frac{r_0{}^{n+1}+B_1{}^n r_0}{B_1{}^n n}\right).$$

Cohesive energy for a number of FCC, BCC and HCP metals is calculated and found to be in good agreement with the experimental results.

Discussions

It is obvious from the inspection of our form of potential that the condition (i) is satisfied. A finite value of cohesive energy as calculated for various substances also satisfies condition (ii). A first hand calculation of elastic constants also satisfies the condition $C_{11}-C_{12} > 0$, both being separately positive.

The choice of the property to be studied at the preliminary stage was dictated by the fact that the cohesive energy of metals has not been studied in detail. Some calculations have been done on alkali and noble metals and as is clear from the data collected in table 1 that our results show much improvement over the results of earlier workers. Moreover, in the most widely used Morse and Rydberg functional form, cohesive energy is chosen as a known quantity in the determination of the parameters of the potential and hence its direct calculation is not possible. As is evident from the form of potential that any uncertainty in the values of ionic radii does not effect our results appreciably. In fact any other

TABLE 1

Substance	Lattice[a,b] constant $\times 10^8$ cm	$\beta^{(c)} \times 10^{12}$ cm^2/dyn.	n	m	Cohesive energy($-\phi_c$)(Kg. Cul/mol		
					Calculated	Experimental[b]	Others[d,e]
Pb	4.9138	2.31	3	12	46.6	47	
Ag	4 068	0.99	4.5	7	72.6	68.3	58.9
Ni	3 5142	0 53	4	6*	107 8	102.3	
Cu	3 6022	0.72	4	7	78.1	80.8	59.9, 83.7
Al	4.0284	1 34	3*	7	73 9	76 9	
Ca	5 5528	5 70	4	6	39.9	42.1	
Sr	6 0534	8 19	4	6	35.7	39 1	
Pd	3.880	0.53	5	6.5	96 5	90.8	
Pt	3.9142	0.36	5 5	8	128.2	135.0	
Au	4 0626	0.57	5.5	8	88.9	87.3	53.3
Li	3 40	8.7	1 5	6	33.8	38.0	
Na	4.2250	15.6	2	6	26.8	26.0	23.2, 25.9
K	5 2250	35.0	2	6	22 8	21.7	27.9, 24.2
Cs	6.0450	67.0	2	6	18.6	19.1	
Mo	3.1432	0.36	5	7	155.7	157.1	
Cr	2 8818	0.52	5	7	83.8	94.5	
Fe	2.8590	0.59	4	7	89.9	98.9	
Zn	2.659**	1.60	5	7	29.9	31.1	
Cd	2 970**	2.41	6	7	22 64	26.76	
Mg	3.190**	2.95	4	6	40.4	35.3	

*Values are changed by unity, **Nearest neighbour distance.

(*a*) Varshni & Bloore, 1963, (*b*) Kittel 1967. (*c*) Kittel 1961, (*d*) Kuhn & Van Vleck 1950, (*e*) Kambe 1955,

choice of B_1 and B_2 will be equally suitable, provided it satisfies the condition

$$\left(\frac{B_{1,2}}{r}\right)^{n_1 m} \quad 1.$$

Palladium which does not find a place in studies of Furth (1944) is also included in this list. In general our calculated values are in good agreement with the experimental data.

It is interesting to note that an excellent agreement is obtained in quite complicated cases, such as platinum and molybdenum etc., with this simple two term potential. Difference in our calculated values from the experimental ones may be partly attributed to the uncertainty in the values of compressibility, which is taken from the work of Furth (1944) and data collected by Kittel (1961), and it is referred to at room temperature. The experimental values of the cohesive energies (Kittel 1967) are also at room temperature

It may be pointed out that a similar logarithmic form for the overlap repulsion, adopted between a pair of atoms in solidified noble gases is found to predict the experimental results fairly well (Behari 1969).

ACKNOWLEDGMENTS

The author is thankful to Dr. B. B Tripathi for useful suggestions and discussions during the course of investigation. He also wishes to express his high sense of gratitude to Prof. Krishnaji for encouraging correspondence. Interest of Mr. S. Prakash in the work is thankfully acknowledged

REFERENCES

Behari J. 1969 (unpublished)
Born M. 1940 *Proc. Cambridge Phil. Soc.* **36**, 160
Cole 1959 *IBM J. Research Develop.* **3**, 126.
Dayal B. & Sharma R. S. 1955 *Proc. Phys. Soc.* **B68**, 1949.
Furth R. 1944 *Proc. Roy. Soc.* **A183**, 87.
Girifalco L. A. & Weizer V. G. 1959 *Phys Rev.* **114**, 687
Kambe K. 1955 *Phys. Rev.* **99**, 419.
Kittel C. 1961 *Introduction to Solid State Physics, (Second Edition) Asia Publishing House*, 99.
1967 „ „ „ „ *(Third Edition), John Wiley and Sons, Inc New York, London, Sydney*, **29**, 78.
Kuhn T. S. & Van Vleck J. H. 1950 *Phys. Rev.* **79**, 382.
Morse P. M. 1929 *Phys. Rev.* **34**, 57.
Mott N. F. & Jones H. 1936 *The Theory and Properties of Metals and Alloys.*
Nikulin V. K. 1966 *Phys. Stat. Solidi* **16**, 125.
Pauling L. 1963 *The Nature of the Chemical Bond, (Third Edition), Cornell University Press* 514.
Prakash S. & J. Behari 1969 *Indian J. Pure Appl. Phys.* **7**, 709.
Rydberg R. 1931 *Z. Physik* **73**, 376.
Seitz F. 1940 *The Modern Theory of Solids, Mc-Graw-Hill Book CompanyInc. New York and London*, 372.